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Innovative method and apparatus for deep cleaning of soluble salts from mortars and lithic materials

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Abstract

A new method improves the quality and durability of decontamination by soluble salts, compared with conventional application of wraps. The salts inside the porous material are brought in solution by soaking with distilled water, then aspired by a suction nozzle applied to the sample surface, allowing the solution to move towards the surface. Finally, the method tested on plaster samples with different suction flows is effective in the cleaning. As every surface to be cleaned could be affected by different extent of deterioration, specific flows of suctions were investigated.

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Keywords: cleaning; soluble salts; porous materials; restoration; salt extraction.

1. Introduction

Inorganic porous materials such as plaster, mortar, concrete, brick and stones employed in monumental structures or in sculptures tend to develop saline efflorescence after their emplacement and during their life cycle [1]. The saline phases that represent some of the concurrent causes of mechanical and chemical deterioration in the host materials are mainly nitrates, carbonates and chlorides [2-9]. The presence of salt crystals on the surface and/or in

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the layers lying immediately under the wall surface can cause problems of preservation of works of art, as for example, fresco paintings, because salts are the main cause of formation of saline efflorescence or sub-efflorescence. Limiting the interaction between porous materials and salts is of primary importance dealing with cultural heritage, in fact artworks such as frescoes and sculptures can be affected by severe damages due to saline contamination.

Capillary rise [10] and damp circulation in masonry [11] are the main causes of salt mobilization and crystallization; their mobility and precipitation reflect cyclic wetting and evaporation, as demonstrated by the concentric aureoles or coronas characteristic of the alteration patterns. Thus, precipitation of progressively more soluble salts from brines suggests that water acts as a selective carrier. Due to stepwise water ingression and salt precipitation, the physical decay of the host material is progressive and infiltration to the core of the material is time, climate- and microtexture-dependent. For these reasons, the occurrence of salts inside the host can attain the deepest and the highest portions from the wetting source. The propagation of secondary porosity is consequent to the failed recovery of the host material.

Current procedures of desalination encompass several applications of cellulose or sepiolite wraps [12]. The procedure requires the application of poultice layer, soaked with distilled water, on the porous material, to be removed after the dry-out process. The process aims at breaking the surface tension of the saline solution (because of the short distance between the pack and the surface of the volume of porous material), thereby creating a so-called bridge that can accelerate the migration, by osmosis and/or capillarity, of the saline solution from the porous material to the pack. The water driving forces allows part of the soluble salts to move from the substrate to the poultice, where they result then trapped. This method however has a very slow dynamic, requiring a very long time for extracting all the saline solution from the volume of porous material. The cleaning takes place over many cycles of soaking and poultice substitution, corresponding to several days; moreover, should the saline solution not completely come out of the porous material, it might stagnate in the wall, thus causing further damage. So the salt removal fails to be shallow and not durable, as often the deeper crystals outcrop after a while.

Furthermore, the wraps and the poultices do not allow controlling whether all the saline solution has been extracted or is still impregnating the porous material.

Extracting a sample of porous material is not always possible or easy, e.g. because the removal of a part of a fresco painting is at any rate a destructive action. In addition, salts may be distributed unevenly in the porous material, that can be uneven itself.

This rationale led us to explore methods to achieve an effective cleaning and salt removal [13]. A new methodology and apparatus was patented by University of Genoa to improve the quality and the durability of decontamination from soluble salts, if compared with the conventional poultices of cellulose pulp and sepiolite. The cellulose pulp is a material used for the production of paper, also employed in the stages of restoration for efflorescence cleaning. Sepiolite is a clay mineral; the two are characterized by high surface/volume and hygroscopic behavior. Our method couples a mechanical treatment (suction) with dilution of salts and refining with wraps.

2. Experimental procedure

2.1. Material

Given the construction materials and techniques used in the past [14], we addressed the main building components, as plaster and stones. In particular, a preliminary experiment was carried out on plaster, which was characterized to describe its main properties. This material has always been used as a cover for masonry walls, therefore affected by the capillary rise in the wall structures and by their same damages [15].

The samples were made in laboratory using a mixture of Po river sand (60% in weight) and slaked lime (40% in weight). The mortar so prepared was poured into circular molds (Ø: 7 cm, thickness: 15 mm) to obtain homogeneous and reproducible specimens.

2.2. Salts contamination: total immersion

The specimens were split in 2 sets, addressed to different extent of saline contamination (Table 1), so as to carry out the cleaning on sample sets with different levels of degradation. Several standard tests are based on total immersion of the sample in a saline solution [16-17], but all of them develop across three stages: immersion, drying and cooling.

The UNI EN 14147 [18] was followed for the saline solution sodium chloride with a degree of purity not less than 95% and distilled water with conductivity less than or equal to 20 mS/cm. The UNI EN 12370 [19] was followed for the sample preparation and for the contamination method.

Initially, the first sample set was dried to constant weight and then, after cleaning and dry, was inserted into a tank and covered with the salt solution up to 8 mm above the upper face of the sample at 24°C room temperature for 2 h (immersion stage). The samples were then placed in a second tank, where each specimen is arranged to be 10 mm far from the other and 20 mm from the wall of the container. Here the specimens were left soaking for 2 h at 20°C temperature. The second step was the drying stage: the samples were extracted from the container and introduced into the heating cabinet at 105°C for 16 h. Finally, the samples were conditioned to 22°-23°C room temperature for 4 h (cooling stage). At the end of each cycle the variations in the sample weight were recorded.

The second sample set was treated with the same standard test, but the immersion step was repeated 5 times to achieve higher contamination. The percentage of salt increase in the material is demonstrated by the rise of sample weight and by conductivity test [20]. Furthermore, on the plaster surface an increase of efflorescence is visible, with respect to the first set.

Table 1. Description of the test procedure on the two sample sets.

Sample set	Type of contamination	N° of cycles	NaCl concentration [weight %]	NaCl in the sample [g/L]
1	Total immersion	2	10	3.82
2	Total immersion	5	10	5.47

2.3. The cleaning method

The method is based on the pressure difference between the inside and the outside. The suction process, in fact, generates a vacuum that accelerates the migration of the substances in (saline) solution from the porous material to the outside, so that they can be collected and removed. The mechanical vacuum comprises: I) a suction head that can be coupled to at least one surface portion of the material to be treated, II) an absorbing element positioned in the suction head so that, when at least a part of the surface of the absorbing element is placed on the sample, it becomes in contact with the surface under treatment III) a suction device in fluidic communication with the suction head, capable of generating a pressure difference between the inside of the head and the inside of the porous material. IV) An apparatus wherein the absorbing element is imbued with a liquid aimed at reducing the surface tension of the solution. A flexible tube connects the pump to an interface nozzle that must be placed upon the surface to be cleaned, which comes in contact with the material. In order to preserve the surface from direct contact with the rigid part of the nozzle, it is provided with a soft sponge that acts as a filter for the salts.

The suction occurs by means of a pump with a range flow from 15 Nm^3/h to 38 Nm^3/h.

The decontamination was controlled by conductivity tests on the sponges and the cleaned samples at the end of treatment.

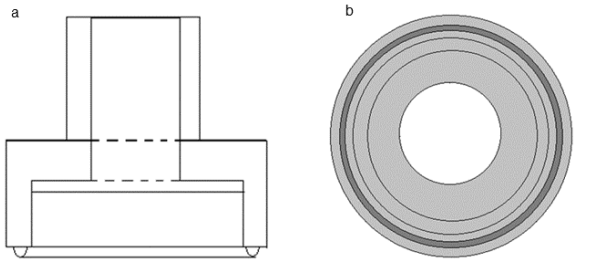


Fig. 1. (a) Cross section of the suction nozzle.; (b) Basal view of the nozzle (bottom up).

The two contaminated sample sets have undergone different cleaning treatments in order to assess the most effective.

2.4. 2.4 Scanning Electron Microscope (SEM) investigation

Samples were characterized by SEM-EDS (Vega 3 LMU Tescan). A Scanning Electron Microscope Tescan Vega 3 LM equipped with an Apollo X detector and Microanalysis TEAM EDS System acquired images and mineral compositions. Microphotographs were carried out on gold–sputter coated 3D samples under variable pressure conditions with backscattered detectors. Semi-quantitative electron microprobe analyses of phases were obtained under high-vacuum conditions by use of natural standards. Operative conditions were: voltage 15 to 20 eV.

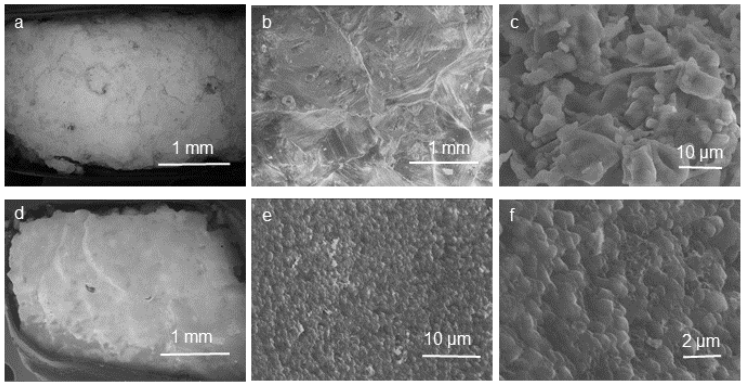


Fig. 2. SEM image (under variable pressure and back scattered electrons detector) of the contaminated sample Set 1; (b) detail of salt crystals on the surface; (c) magnified detail of NaCl crystals; (d) SEM image of the cleaned sample; (e) detail of the clean surface; (f) magnified sample surface.

The electron microscopy imaging allowed investigating the surface of the sample before and after treatment (Fig. 2). The analytical runs confirmed that the cleaning method has removed the NaCl crystals from the sample surface.

3. Results and discussion

The effectiveness of the procedure was demonstrated by conductivity measures on samples and sponges used for the cleaning tests.

Previously, the intrinsic conductivity of the plaster sample without salts was assessed. Each sample was milled and placed in distilled water (< 2µS), so as to obtain by difference the value of the contaminated and the cleaned samples.

In addition, the conductivity test was also carried out on the 26 sponges used for the cleaning treatment; each sponge was soaked in 150 ml of distilled water (< 2µS) and its conductivity measured. The sponge after the first suction has a higher conductivity value, continuously decreasing (Fig. 3). This proves that for each treatment, the sample is gradually cleaned, until the conductivity value of the blank sample (without salt) is reached.

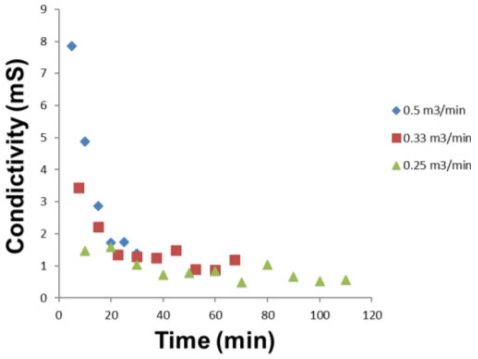


Fig. 3. Sponge conductivity vs. time.

The sample Set 1 (NaCl 3.82 g/L) was treated with the mechanical vacuum at different flow suctions and for different time (Fig. 4). Three samples were cleaned with suction flow at 0.25 m^3/min (slow speed), three others were treated at 0.33 m^3/min (medium speed) and the last at high speed (0.50 m^3/min).

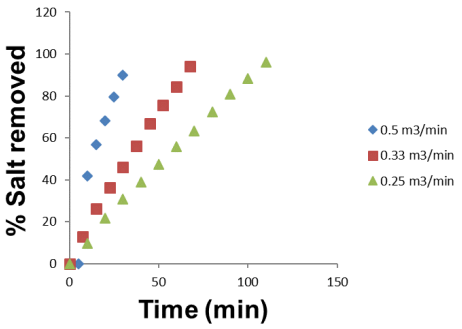
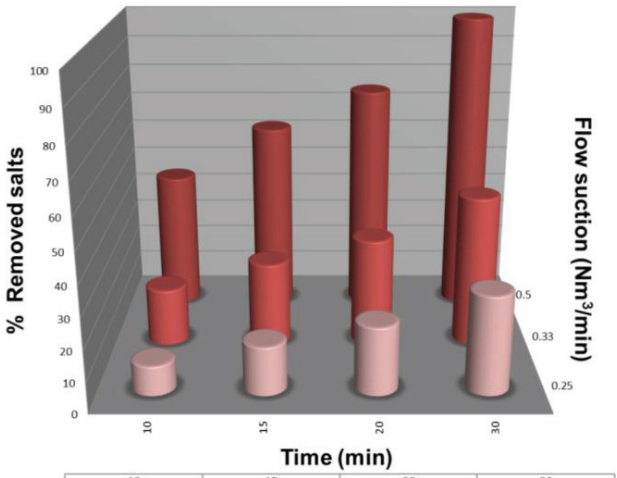


Fig. 4. Correlation of the three different speed suction applied on Set 1 with % removed salt.



	10	15	20	30
0.5	45.43	62.66	75.46	99.76
0.33	18.9	27.68	35.7	49.82
0.25	9.66	15.91	22.19	32.11

Fig. 5. Flow suction speed, time and % removed salts for sample Set 1.

The 0.5 m^3/min flow suction speed provides the maximum salt removal/time (Fig. 5). In 30 minutes the total salts removal was obtained, by performing 6 suctions of 5 min each. The treatment needs to be interrupted, as the contact surface becomes dry, so each 5 minutes the surface was nebulized with distilled water, to constantly keep the NaCl in solution.

The same procedure steps were performed on the second set of plaster samples, Set 2 (NaCl 5.47 g/L). The specimens were wet with distilled water and cleaned with a 0.5 m^3/min suction flow (Fig. 6).

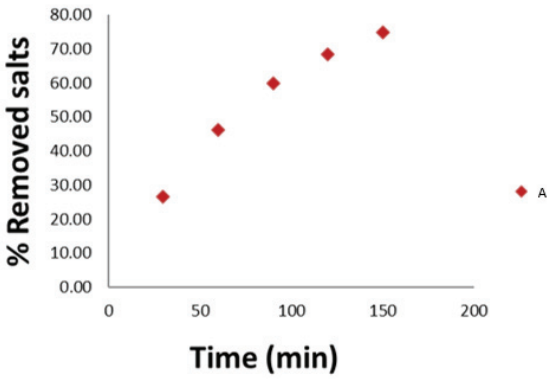


Fig. 6. Percentage of removed salts versus time for sample Set 2.

In this case, the salts contamination was higher than the Set 1, thus it was necessary to perform a 5 treatments to obtain the total removal of salts. The samples underwent suction cycles of 30 minutes each (splitted in six step of 5 minutes) that were repeated for 5 times for a total 150 minutes of suction.

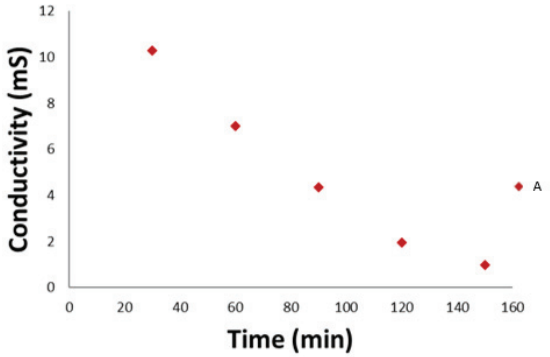


Fig. 7. Conductivity decrease vs. time in sample Set 2.

After each cleaning step, the continuous decrease in measured conductivity highlights the improvement in salt removal until total cleaning is reached (Fig. 7). The quality of cleaning was also demonstrated by the decreasing roughness of the surface due to the uprise and precipitation of salt crystals, and the recovery of the pristine aspect. In the case of frescoes, this is particularly evident (Fig. 8).

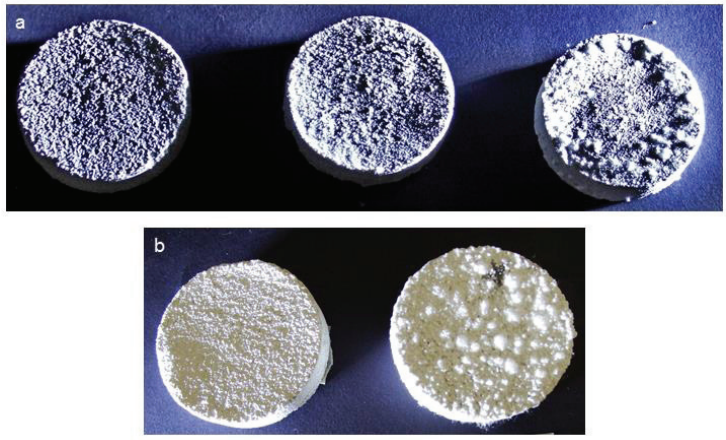


Fig. 8. (a) Three samples under sidelight, evidencing the progressive cleaning of surfaces, from right to left. (b) Magnified detail of treated (left) and untreated (right) sample.

Laboratory experiments therefore support that the mechanical vacuum method is fast and much deeper than wraps or poultices. However, in terms of intervention on real art pieces, or historical buildings, a preliminary investigation of the porosity network and of possible development of the secondary porosity during salt impregnation is necessary, to modulate the velocity of subtraction of a solid, though temporary, component of the host material. An extensive diagnostic approach of the salt host is therefore useful to evaluate the microtexture and the resilience of the material to restoration.

4. Conclusions

The tests carried out on plaster samples have shown that the method patented by University of Genoa is effective in the cleaning of this porous material. A preliminary experiment on fresco samples established that the cleaning with only adsorbent wraps was not effective for the deep salt removal in the material and operated just a shallow

cleaning, so that soluble salts were liable to emerge later as efflorescence. The method was effective for salts removal from plaster and it can be coupled with traditional methods to achieve a long lasting result. In fact, following the treatment with the aspirating nozzle, an optimal finishing can be obtained with the extraction of very shallow salts by sepiolite and/or cellulose wraps.

Among the several suction flow conditions experimented, the best quality to time ratio was obtained under the 0.5 m^3/min, i.e. the fastest one. Under real conditions, the surface to be addressed for cleaning could show different extent of weathering, as a consequence others suction flows can be applied for treatments that need the interaction with the surface to be very soft.

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